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## DIVISION S-5—PEDOLOGY

### Spatial Distributions of Soil Chemical Conditions in a Serpentinic Wetland and Surrounding Landscape

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#### ABSTRACT

Soils formed from serpentinite contain an abundance of Fe, Mn, Cr, Ni, and Mg, and low concentrations of the plant-essential nutrients Ca and K. The resulting vegetation is commonly xeromorphic and characteristically stunted. This study was conducted to (i) determine the spatial distributions of heavy metals and exchangeable cations ( $M_e$ ) in an ultramafic wetland and surrounding landslide terrain, and (ii) to interpret the distributions relative to environmental conditions and pedogenic processes on the component landscape positions. Distributions of dithionite-extractable metals ( $M_d$ ) and  $M_e$  in surface soils (0–15 cm depth) were assessed by kriging and by landscape units, characteristic landscape position, soils, and vegetation. Abundance of  $M_e$ s ranked in the following order:  $Mg > Ca \gg K > Mn > Na > Ni$ . The Ca/Mg ratios range from 0.13 to 3.77 (mean 0.43), with the highest ratios in a landscape unit with nonserpentine metamorphic colluvium over serpentinitic residuum. Exchangeable cations are concentrated within the wetland relative to surrounding terrain. Dithionite-extractable Fe, Mn, and Ni are concentrated in soils on the oxidizing, nonhydric lower landscape positions, near the hydrologic discharge point of the wetland. Chromium and Al are concentrated in the nonhydric upper landscape positions. Due to reducing conditions, the wetland contains low concentrations of  $M_d$  relative to the surrounding nonhydric terrain. Large vegetation differences between moisture class coupled with moderate vegetation differences between landscape units within the same moisture class, suggest that vegetation occurrence within the study area is controlled primarily by hydrology, and secondarily by elemental conditions.

ULTRAMAFIC ROCKS OCCUPY a small portion (<1%) of the earth's land surface, but are locally abundant in ophiolite belts along tectonic plate margins (Brooks,

1987; Coleman and Jove, 1991). In North America, ultramafic rocks form two discontinuous bands along the east and west side of the continent. Of these, the largest area of ultramafic terrain is in the Klamath Mountains province of northern California and southern Oregon (Irwin, 1977).

Serpentinite is a metamorphic rock formed from the low temperature (300–600°C) hydrothermal alteration of igneous ultramafic rocks (O'Hanley, 1996). These rocks are generally classified as peridotite, common varieties of which are dunite, harzburgite, and lherzolite (Wyllie, 1967; Coleman, 1971; Moores, 1973). The major minerals are olivine, orthopyroxene, clinopyroxene, and chromite (Moody, 1976). Quartz is absent and feldspar is minor or absent in all of these rocks (Ehlers and Blatt, 1982). Most ultramafic rocks have been partially hydrated or completely serpentinized (Moody, 1976). Nearly all serpentinite masses are serpentinized peridotites that have been tectonically emplaced along continental margins (Coleman and Jove, 1991). Serpentine minerals (antigorite, lizardite, and chrysotile) are the predominant minerals in serpentinite, while magnetite, brucite, and Mg- and Ca-aluminosilicates are common accessory minerals (O'Hanley, 1996).

Total elemental analysis of peridotites and serpentinites from the Klamath Mountains show low Ca and Al, and extremely low or no measurable K (Table 1). Potassium is a trace element in ultramafic rocks with total concentrations on the order of 200 mg kg<sup>-1</sup> (Goles, 1967). Ultramafic rocks are noted for their elevated levels of heavy metals compared with more common aluminosilicate rocks.

Soils formed from ultramafic rock are strongly influenced by the geochemistry and mineralogy of the parent material. Common constituents of ultramafic soils in-

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**Abbreviations:** e [subscripted], exchangeable cation; d [subscripted], dithionite extracted metal; CEC, cation-exchange capacity; ICP-OES, inductively coupled Ar plasma optical emission spectroscopy

**Table 1. Selected elements in ultramafic rocks from the Klamath Mountains.<sup>†</sup>**

|              | Si                 | Al | Mg  | Ca | Fe | K |
|--------------|--------------------|----|-----|----|----|---|
|              | g kg <sup>-1</sup> |    |     |    |    |   |
| Peridotite   | 201                | 3  | 273 | 8  | 67 | 0 |
| Serpentinite | 189                | 3  | 239 | 9  | 69 | 0 |

<sup>†</sup> Data summarized from Quick, 1981; Graham et al., 1990.

clude serpentine minerals, magnetite, Fe oxides (goethite, hematite, and maghemite), smectite, and chlorite. The abundance of Mg released from serpentine weathering makes it the dominant cation on soil exchange sites, leading to the characteristically low exchangeable Ca/Mg ratios (Brooks, 1987). The Ca/Mg ratio is typically higher in A horizons (~1.0) than in subsoils (~0.1) (Rabenhorst et al., 1982; Alexander et al., 1989; Graham et al., 1990). Exchangeable cation data from 23 soils in the Klamath Mountains indicate consistently low levels of K (0.0–1.1 cmol<sub>c</sub> kg<sup>-1</sup>) because of the lack of K-bearing minerals, and variable Ca (0.7–21 cmol<sub>c</sub> kg<sup>-1</sup>) and Mg (1.1–29 cmol<sub>c</sub> kg<sup>-1</sup>) concentrations (Alexander et al., 1989; Graham et al., 1990). Although concentrations of Ca and Mg varied across soil profiles, Ca/Mg ratios (0.1–5.9) always decreased below the A horizon, often by an order of magnitude. Soils on the Trinity serpentinized peridotite have pH values mostly between 6 and 7, typically increasing with depth (Alexander et al., 1989).

Serpentine vegetation (collectively referring to vegetation on ultramafic rocks) is typically sparse, and biomass productivity is low in comparison to that on soils derived from more felsic rocks. Many researchers attri-

bute poor plant growth in serpentinitic terrain to the abundance of Mg and Ni (Brooks, 1987). In addition to Mg and Ni abundance, Kram et al. (1997) suggested that K deficiency is responsible for poor productivity of a forested catchment in serpentinitic terrain in the Czech Republic. Alexander et al. (1989) identified a significant relationship between Ca/Mg ratios in surface soils and timber yield index in the Klamath Mountains. Elevated Ca levels in surface soils have been attributed to biocycling (Hausenbuiller, 1972; Rabenhorst et al., 1982; Alexander et al., 1985; Graham et al., 1990; Kram et al., 1997), but in southeastern Pennsylvania, Barton, and Wallenstein (1997) attributed high Ca/Mg ratios under individual Virginia pine (*Pinus virginiana* P. Mill.) to increased leaching of Mg, not biocycling of Ca. These researchers suggest that root growth increased parent material weathering, resulting in better drainage and increased Mg leaching.

According to Kruckeberg (1984), California contains the richest diversity of serpentine vegetation among all temperate regions worldwide. In the Klamath Mountains, serpentine indicator species include Jeffrey pine (*Pinus jeffreyi* Grev. and Balf.), incense cedar [*Calocedrus decurrens* (Torr.) Florin], and shrubby species of the genera *Ceanothus* (Kruckeberg, 1984).

Previous studies have evaluated chemical and mineralogical properties of serpentinite-derived pedons or horizons (Rabenhorst et al., 1982; Alexander et al., 1989; Graham et al., 1990; Bulmer and Lavkulich, 1994; Gasser et al., 1995), but there is little information concerning the spatial distribution of chemical properties across

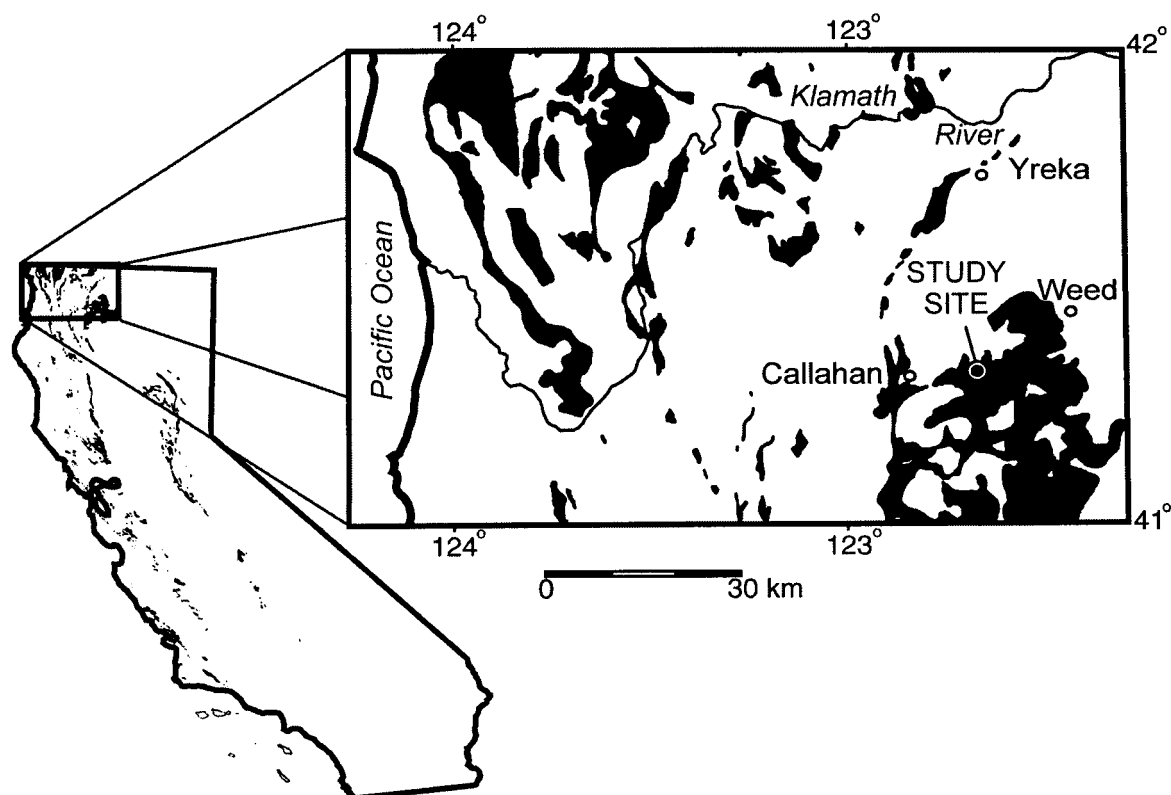


Fig. 1. Location of study area and distribution of serpentine in northwestern California and throughout the state.

serpentine landscapes. This study was conducted to (i) determine the spatial distributions of heavy metals and  $M_e$  in an ultramafic wetland and surrounding landslide terrain and (ii) to interpret the distributions relative to environmental conditions and pedogenic processes on the component landscape positions.

## MATERIALS AND METHODS

### Environmental Setting

The study site is in the Klamath Mountains physiographic province within the Trinity ophiolite in southwestern Siskiyou County, CA (Fig. 1). This ultramafic body, the largest in the Klamath Mountains, is composed primarily of olivine-rich, serpentinized peridotite with minor inclusions of dunite, plagioclase-bearing peridotite (2–10% Ca-plagioclase), and pyroxenite (Lipman, 1964; Quick, 1981; Peacock, 1987). Metamorphic alteration minerals within the rocks include serpentine (antigorite, lizardite, and chrysotile), talc, tremolite, chlorite, and magnetite (Lipman, 1964). Fine-grained ( $\leq 20 \mu\text{m}$ ) calcite, dolomite, and magnesite are commonly disseminated as trace components throughout the serpentinized peridotite (Peacock, 1987).

Specifically, the study site is in the Scott Mountains, where mass wasting and fluvial erosion are the main geomorphic processes, and landslides are common in steep areas (Miles and Goudey, 1997). The soils of the study site were previously mapped (1:62 500) as Mollic Haploxeralfs formed from serpentinized peridotite. Typic Haploxeralfs and Ultic Haploxeralfs formed from nonserpentine metamorphic rock occur

about 100 m south of the study area (Foster and Lang, 1994). The study site has an elevation ~1200 to 1240 m. The climate is Mediterranean with an average annual precipitation of 1000 mm (Rantz, 1968) falling as rain and snow, predominantly (>90%) between October and May (Foster and Lang, 1994).

The site was selected because it contained a range of landscape positions and hydrologic conditions within a geographically small area (~3.2 ha). The area consists of a landslide bench and an associated scarp and flanks formed from a rotational slump (Fig. 2). The ponded water behind the slump block is maintained by groundwater flow, several springs, ephemeral streams, and overland water flow in the early spring. The headwaters of the inlet streams to the wetland originate in ultramafic terrain, and the outlet streams drain into Mule Creek, a tributary of the East Fork Scott River (Foster and Lang, 1994). The slopes surrounding the stabilized bench (scarp and flanks) have gradients ranging from 28 to 32%, and are mantled by moderately-deep to shallow, loamy to fine textured soils, and rock outcrops of serpentinized peridotite, while the landslide deposit (foot and bulge) has deep clayey soils with slopes ranging from 3 to 16%. In recent years, the site has been selectively logged and is grazed seasonally by cattle (*Bos taurus*).

### Field Methods

A large portion of the study area is a jurisdictional wetland. As described in the National Food Security Act Manual (Soil Conservation Service, 1994) and the Corps of Engineers Wetlands Delineation Manual (Environmental Laboratory, 1987), a combination of three criteria defines a jurisdictional wetland: hydrophytic vegetation, hydrology, and hydric soils. Hydro-

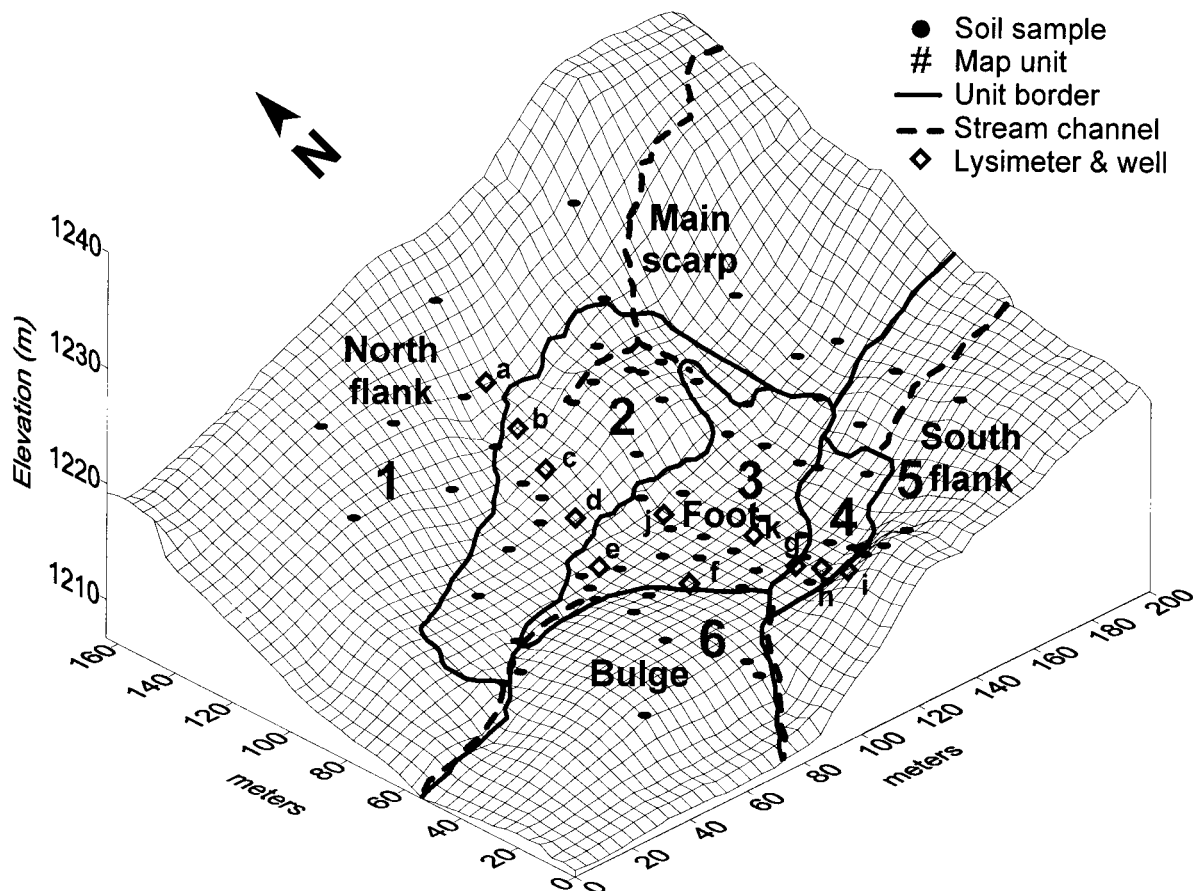


Fig. 2. Block diagram of field area showing geomorphic features, landscape unit boundaries, and sampling locations.

**Table 2. Soil classification, geomorphic position, and moisture condition of map units.**

| Landscape Unit | Soil classification   | Parent material         | Landslide element†       | Slope position  | Predominant slope | Soil texture         | Moisture condition‡ | Vegetation   |
|----------------|---|-------------------------|--------------------------|-----------------|-------------------|----------------------|---------------------|--|
| 1              | clayey-skeletal, magnesian, superactive, mesic Typic Argixerolls (clayey-skeletal, magnesian, superactive, mesic Aquic Argixerolls on footslopes) | colluvium over residuum | scarp and north flank    | back slope      | %<br>30           | 1–15 cm<br>clay loam | xeric               | Jeffrey pine ( <i>Pinus jeffreyi</i> ), incense cedar ( <i>Calocedrus decurrens</i> ), buck brush ( <i>Ceanothus cuneatus</i> ), Idaho fescue ( <i>Festuca idahoensis</i> )  |
| 2              | fine, magnesian, superactive, mesic Cumulic Endoaquolls   | colluvium               | northern portion of foot | toeslope        | 16                | clay                 | aquic, hydric       | rushes ( <i>Juncus</i> spp.), Kentucky bluegrass ( <i>Poa pratensis</i> ), tall fescue ( <i>Festuca arundinacea</i> ), summer clover ( <i>Trifolium longipes</i> ), oatgrass ( <i>Danthonia californica</i> ), yarrow ( <i>Achillea lanulosa</i> ) |
| 3              | fine, magnesian, superactive, mesic Cumulic Endoaquolls   | alluvium, colluvium     | foot                     | toeslope, basin | 8                 | clay                 | aquic, hydric       | sedges ( <i>Carex</i> spp.), bulrush ( <i>Scirpus microcarpus</i> )  |
| 4              | fine, magnesian, superactive, mesic Cumulic Endoaquolls   | colluvium               | southern portion of foot | toeslope        | 8                 | clay                 | aquic, hydric       | sedges, bulrush, horsetail ( <i>Equisetum</i> sp.)   |
| 5              | loamy-skeletal, magnesian, superactive, mesic Typic Haploxeralfs  | colluvium over residuum | south flank              | back slope      | 22                | loam                 | xeric               | ponderosa pine ( <i>Pinus ponderosa</i> ), Douglas fir ( <i>Pseudotsuga menziesii</i> ), white fir ( <i>Abies concolor</i> ), incense cedar, Rose ( <i>Rosa</i> sp.), prince's pine ( <i>Chimaphila umbellata</i> )                                |
| 6              | clayey-skeletal, magnesian, superactive, mesic Pachic Argixerolls   | colluvium               | bulge                    | summit          | 3                 | clay loam            | xeric               | ponderosa pine, incense cedar, buck brush, California fescue ( <i>Festuca californica</i> )  |

† Terminology from Selby (1993).

‡ xeric = dry in all parts of soil moisture control section for 45 or more consecutive days in the 4 months following the summer solstice and moist in all parts for 45 or more consecutive days following summer solstice (Soil Survey Staff, 1998); aquic, hydric = conditions of inundation or saturation that last long enough during the growing season to develop anaerobic conditions within 30 cm of soil surface (Vepraskas and Sprecher, 1997).

phytic vegetation is macrophytic plant life capable of growth in substrates that are at least periodically deficient in O<sub>2</sub> as a result of high water content (National Research Council, 1995). Hydric soils are defined as soils that formed under conditions of saturation, flooding, or ponding long enough during the growing season to develop anaerobic conditions in the upper part (Federal Register, 1994). Wetland hydrology criteria require a water table within 30 cm of the soil surface for a continuous period for >5% of the growing season in one out of every two years (Environmental Laboratory, 1987; National Research Council, 1995).

The wetland within the study area was delineated according to the criteria listed above. The vegetation was distinguished in early May 1998, using Hickman (1993) and Vitt et al. (1988), and wetland species were identified by using the Western Wetland Species List (Soil Conservation Service, 1985). Hydric soils were identified according to hydric soil indicators (USDA, 1996; Bell and Richardson, 1997). The hydrology was interpreted from geomorphic setting (Brinson, 1993) and direct observation of the water table on the surface, and by wells in the transition zone between the inundated region of the landslide and the dry upslope positions (Fig. 2). Lateral flow and surface runoff from snowmelt in the winter and spring are the predominant sources of water in the wetland. Two streams above the wetland bring a considerable amount of water to the wetland in peak snowmelt periods. Two outlet streams drain the wetland, located on the north and the south side of the bulge. The north outlet stream is the primary drainage, evident by its lower elevation (Fig. 2).

Seventy surface soils (0- to 15-cm depth) occupying a variety of geomorphic positions were sampled by excavation with a tile spade. Landscape units (Fig. 2) were delineated based on vegetation, topography, soils, and landscape position. Soil

classifications, geomorphic positions, vegetation, and moisture conditions of the landscape units are described in Table 2. Results will be presented and discussed with reference to landscape units.

A topographic survey of the area was prepared with a total station (Model No. Constructor DC-5, Spectra-Physics Laserplane, Inc., Dayton, OH), with an average sampling density of one elevation point per 7.5 m<sup>2</sup>. Surface maps were created by kriging data with SURFER Ver. 6 (Golden Software, Inc., Golden, CO). A block diagram constructed from the surface maps showing geomorphic features and sampling locations is in Fig. 2.

Porous cup suction lysimeters and wells were installed on a variety of landscape positions (Fig. 2). Within Units 3 and 4, lysimeters were installed at 30-, 60-, and 90-cm depths. Lysimeters were installed at 60-, 90-, and 120-cm depths in Unit 2. Soil water chemistry, stream water chemistry, and water table depths were monitored seasonally (March, June, September, December) in 1996 and 1997. Stream water samples were collected from the inlet and outlet streams ~20 to 30 m from the wetland. Soil water samples were collected with a pressure vacuum hand pump (Model no. 2005G2, Soil Moisture Equipment Corp., Santa Barbara, CA) at 5500 kPa of soil suction. All water samples were stored in polyethylene bottles, and transported on ice to the laboratory where they were kept at 4°C until analyzed.

### Landscape Unit Descriptions

**Unit 1: North Flank and Scarp.** Soils in this unit are Argixerolls, with some Haploxeralfs on the shoulderslope of the north flank. The main scarp contains an ephemeral stream that diffuses into the wetland near the border of Unit 2 and Unit

1. The soils within Unit 1 are formed from colluvium over residuum. Slopes are ~30%. The entire unit contains outcrops of serpentinized peridotite. The dominant vegetation in the unit consists of serpentine indicator species: incense cedar, Jeffrey pine, buck brush [*Ceanothus cuneatus* (Hook.) Nutt.], and Idaho fescue (*Festuca idahoensis* Elmer).

**Unit 2: North Portion of Foot.** This is the northern toeslope within the wetland. The soils are Endoaquolls. These hydric soils formed from colluvial sediments that have filled in the scar of the landslide behind the bulge. The slopes on the unit are ~16%. The vegetation is dominated by three plant community types that vary with hydric condition of the soil. In the area nearest Unit 3, the plant community consists of rushes (*Juncus parryi* Englm., *Juncus bufonius* L.). In the drier areas, the plant community contains Kentucky bluegrass (*Poa pratensis* L.), tall fescue (*Festuca arundinacea* Schreb.) and long-stalk clover (*Trifolium longipes* Nutt.). In the very driest portions of the unit, oatgrass (*Danthonia californica* Bol.) and yarrow (*Achillea lanulosa* Nutt.) dominate.

**Unit 3: Foot.** This area is inundated at the soil surface throughout the year. The soils are Endoaquolls formed in hydric moisture conditions in colluvium and alluvium that has accumulated behind the bulge. Slopes in the unit are ~8%. The vegetation is dominated by *Carex* spp. and inclusions of small-fruit bulrush (*Scirpus microcarpus* J. & K. Presl.).

**Unit 4: Southern Portion of Foot.** This area is also inundated at the soil surface throughout the entire year. The soils are Endoaquolls (hydric moisture conditions) formed in colluvium that has accumulated behind the bulge. Slopes in the unit are ~8%. The vegetation includes rushes, clover, and mosses (*Hypnum* spp., *Pohlia* spp.).

**Unit 5: South Flank.** The south flank is mantled by Haploxeralfs and has several springs near the footslope at the border with Unit 4. The soils formed from colluvium over residuum. The slopes are ~22%. There is a shallow ephemeral stream that diffuses into the wetland near the border of Unit 4 and Unit 5. Unit 5 is dominated by ponderosa pine (*Pinus ponderosa* Dougl. P. & C. Lawson) and Douglas fir [*Pseudotsuga menziesii* (Mirb.) Franco.], with lesser amounts of incense cedar, and white fir [*Abies concolor* (Gord. & Glend.) Lindl. ex Hildebr.]. The understory is mostly *Rosa* spp. and prince's pine (*Chimaphila umbellata* L. W. Bart).

**Unit 6: Bulge.** The soils in this area are Argixerolls formed from landslide colluvium on 3% slopes. The bulge is a convex landscape element that serves as a dam, maintaining a high water table in the wetland. Outlet streams at the northern and the southern borders of Unit 6 drain the wetland. The northern outlet stream serves as the major drainage for the wetland, while the southern outlet only drains the wetland in the winter and spring during peak snow melt. The dominant vegetation in this unit includes ponderosa pine, incense cedar, buck brush, and California fescue (*Festuca californica* Vasey).

### Laboratory Methods

All soil samples were air dried and sieved to obtain the fine earth fraction (particles <2 mm) for chemical analyses (Soil Survey Staff, 1993). Total C was determined by dry combustion (Model no. NA 1500 Series 2, Carlo-Erba Instruments, Milan, Italy) (Nelson and Sommers, 1996). The pH was determined on 1:1 soil/water mixtures. Exchangeable cations ( $\text{Ca}_e$ ,  $\text{Mg}_e$ ,  $\text{Na}_e$ ,  $\text{K}_e$ ,  $\text{Mn}_e$ ,  $\text{Fe}_e$ ,  $\text{Cr}_e$ ,  $\text{Ni}_e$ ,  $\text{Al}_e$ ) were extracted from the <2 mm fraction with 1 M ammonium acetate at pH 7.0, and their concentrations determined by inductively coupled Ar plasma optical emission spectroscopy (ICP-OES). Cation-exchange capacity was calculated by sum of  $\text{M}_e$ . Citrate-dithionite extraction (Holmgren, 1967) was used to as-

sess the secondary oxyhydroxide forms of Fe ( $\text{Fe}_d$ ), Mn ( $\text{Mn}_d$ ), and associated elements,  $\text{Al}_d$ ,  $\text{Cr}_d$ , and  $\text{Ni}_d$ . Metal concentrations were determined by ICP-OES. The concentration of Mn and Fe in the soil water was determined by ICP-OES.

## RESULTS

### Total Carbon, Cation-Exchange Capacity, and pH

Throughout the study area, C contents of the soils ranged from 1.3 to 21.1%. On average, soils in Unit 4 contain the highest concentration of C (Fig. 3) (mean 14.6%), significantly higher than any other landscape unit (Table 3). The highest CEC values are in the lower landscape positions of Units 3 and 4 near the border of Unit 6 (Fig. 4). The mean CEC values of Units 3 (49.3  $\text{cmol}_c \text{ kg}^{-1}$ ) and 4 (53.6  $\text{cmol}_c \text{ kg}^{-1}$ ) are significantly higher than those of the upslope Units 1 (32.7  $\text{cmol}_c \text{ kg}^{-1}$ ) and 5 (22.0  $\text{cmol}_c \text{ kg}^{-1}$ ) (Table 3). The soil pH is lowest on the upper slopes of Unit 5 (Fig. 5). Within Unit 5 the mean pH is 5.6, significantly lower than the pH in Units 1, 2, and 3 (Table 3).

### Exchangeable Cations

Calcium and Mg are the dominant cations on the exchange sites in all units. Calcium saturation percentage is highest in Units 4 (36.7%) and 5 (53.8%) (Table 3). The total of  $\text{Na}_e$ ,  $\text{K}_e$ ,  $\text{Mn}_e$ ,  $\text{Al}_e$ , and  $\text{Ni}_e$  make up <4% of the cations on the CEC. The concentrations of  $\text{Na}_e$  (0.0–1.2  $\text{cmol}_c \text{ kg}^{-1}$ ),  $\text{K}_e$  (0.1–2.1  $\text{cmol}_c \text{ kg}^{-1}$ ),  $\text{Cr}_e$  (< 0.01  $\text{cmol}_c \text{ kg}^{-1}$ ), and  $\text{Mn}_e$  (0.0–4.7  $\text{cmol}_c \text{ kg}^{-1}$ ) are low and not significantly different between landscape units. Nickel<sub>e</sub> reaches highest concentrations in Units 3 and 6 (Fig. 6), although in Unit 6 (mean 0.06  $\text{cmol}_c \text{ kg}^{-1}$ ) it is significantly higher than in Units 4 (mean 0.01  $\text{cmol}_c \text{ kg}^{-1}$ ) and 5 (mean 0.01  $\text{cmol}_c \text{ kg}^{-1}$ ) (Table 3). The  $\text{Al}_e$  in Unit 5 (mean 0.06  $\text{cmol}_c \text{ kg}^{-1}$ ) is significantly higher than in all other units (<0.01  $\text{cmol}_c \text{ kg}^{-1}$ ) (Table 3).

### Dithionite-Extractable Metals

Dithionite-extracted Mn is concentrated in Unit 6 (mean 3712  $\text{mg kg}^{-1}$ ), near the border of Unit 3 (1729  $\text{mg kg}^{-1}$ ) (Fig. 7). The mean concentration of  $\text{Mn}_d$  in Unit 3 is high, but not significantly distinguished from that in any other unit; however,  $\text{Mn}_d$  concentration in Unit 6 is significantly larger than in Units 1, 2, 4, and 5 (Table 3). Nickel<sub>d</sub> is also concentrated in Unit 6 (mean 570  $\text{mg kg}^{-1}$ ) near the boundary of Unit 3 (mean 483  $\text{mg kg}^{-1}$ ) (Fig. 8), however  $\text{Ni}_d$  concentration is not significantly different among Units 1, 2, 3, and 6 (Table 3). The  $\text{Ni}_d$  concentrations in soils of Units 4 and 5 are ~6 to 10 times lower than in the other units (Table 3).

The highest concentrations of  $\text{Fe}_d$  are found in Unit 6 (mean 22713  $\text{mg kg}^{-1}$ ) near the boundary of Unit 3 (mean 21475  $\text{mg kg}^{-1}$ ) (Fig. 9). The mean concentration of  $\text{Fe}_d$  is not significantly different among all units, with the exception of Unit 4, which has two to three times less  $\text{Fe}_d$  than the other units (Table 3). The mean concentration of  $\text{Cr}_d$  is highest in Units 1 (240  $\text{mg kg}^{-1}$ ) and 6 (200  $\text{mg kg}^{-1}$ ) (Fig. 10), which are among the driest

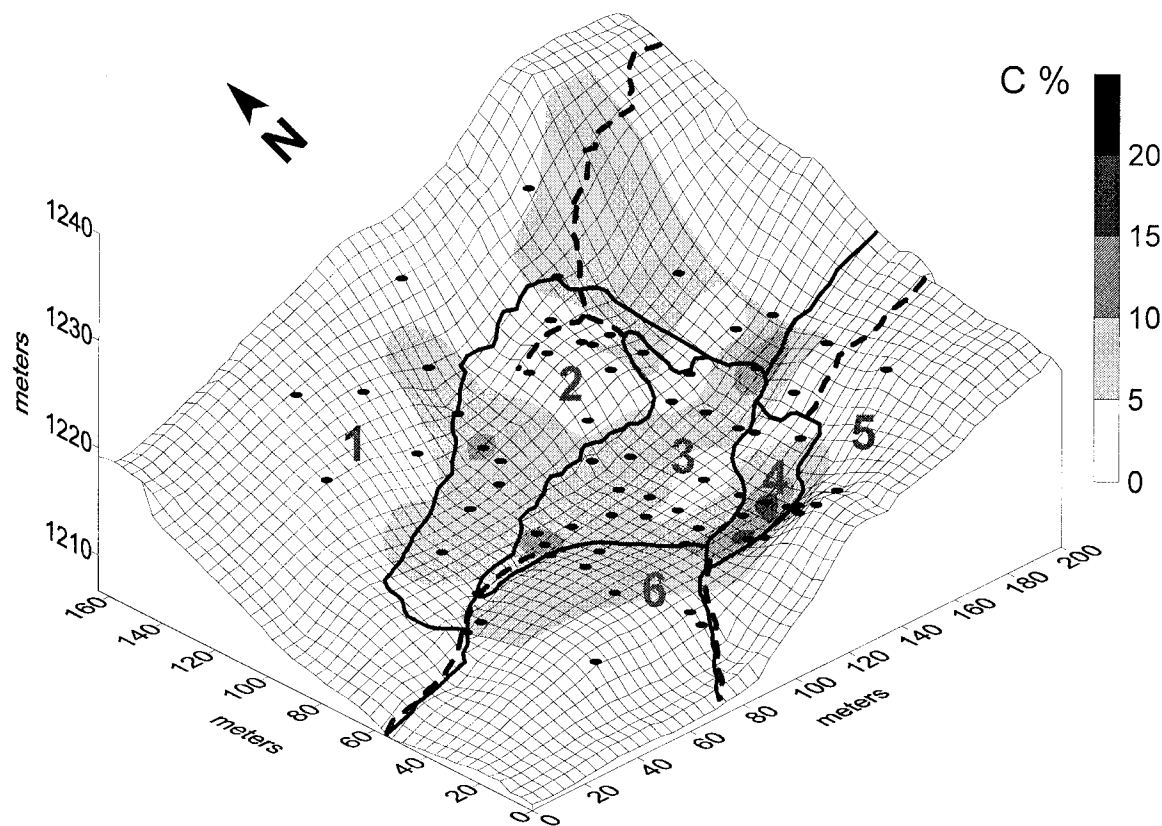


Fig. 3. Spatial distribution of total C in surface soils.

landscape units. Lowest concentrations of  $\text{Cr}_d$  are in Units 2 ( $99 \text{ mg kg}^{-1}$ ), 4 ( $86 \text{ mg kg}^{-1}$ ), and 5 ( $75 \text{ mg kg}^{-1}$ ). Aluminum<sub>d</sub> is concentrated in the dry regions of the study area (Units 1, 5, and 6), while the lowest concentrations are in the wet areas (Units 2, 3, and 4) (Fig. 11).

### Soil Solution

Manganese is highest in lysimeters e, f, and k (Unit 3), and g (Unit 4) located near the border of Unit 6. Iron concentrations are highest in lysimeters e, f, and k (Table 4).

## DISCUSSION

### Parent Material Influence

Unit 1 (north flank and scarp) and 5 (south flank) are on similar geomorphic positions (Table 2), yet they possess different soil chemical properties. Unit 1 has a significantly higher pH, higher exchangeable Mg percentage, lower Ca/Mg ratio, and higher concentrations of  $\text{Cr}_d$  and  $\text{Ni}_d$  (Table 3). Differences in chemical properties between soils can be attributed to mineralogical differences in parent materials. The source of Ca within the study area has been identified as hornblende and tremolite (Lee, 1999), however the distribution of these Ca-bearing amphiboles is not uniform throughout the landscape. The surface horizon of Unit 5 contains ~1.5 fold more amphibole relative to Unit 1 (Lee et al., 1998). Serpentine was not present in the medium silt and clay

fractions of soil horizons derived from colluvium (upper 54 cm) in Unit 5, but was in those derived from the underlying residuum. The lack of serpentine and the abundance of amphibole in the surface of Unit 5 indicate that the colluvium is not of serpentinitic origin. The source of the colluvium may be the metamorphic parent material of the Typic Haploxerept–Ultic Haploxeralf association that is mapped ~100 m south of the study area (Foster and Lang, 1994). The nonserpentine parent material also accounts for lower levels of heavy metals (Cr and Ni) and higher exchangeable Ca/Mg ratios in soils of Unit 5 compared to Unit 1.

### Exchangeable Cations

Magnesium dominates the cation-exchange of all soils but those of nonserpentinitic Unit 5 (Table 3). The predominance of Mg on exchange sites is typical for serpentinitic soils, but biocycling leads to an increase of Ca/Mg ratios in surface soils (Cleaves et al., 1974; Rabenhorst et al., 1982).

Similar  $\text{K}_e$  and  $\text{Na}_e$  values have been previously reported in serpentinite-derived soils (Alexander et al., 1989; Graham et al., 1990). These elements are low because of their low concentration in the parent rock (Table 1).

Exchangeable Al is low throughout the study site, but is highest in Unit 5 (mean  $0.06 \text{ cmol}_e \text{ kg}^{-1}$ ) (Table 3). Exchangeable Al concentrations in serpentinitic soils are low relative to nonserpentinitic soils (Graham et al., 1990), and have been considered to be insignificant

**Table 3. Soil chemical properties (0–15 cm) by map unit (mean and range)†.**

| Chemical parameter  | Statistic | Map unit      |               |              |              |              |              | Total (n = 70) |
|---|-----------|---------------|---------------|--------------|--------------|--------------|--------------|----------------|
|   |           | 1 (n = 10)    | 2 (n = 18)    | 3 (n = 23)   | 4 (n = 5)    | 5 (n = 8)    | 6 (n = 6)    |                |
| %C‡   | mean      | 4.5b          | 5.7b          | 7.1b         | 14.6a        | 3.5b         | 4.5b         | 6.3            |
|   | range     | 2.0–9.1       | 2.8–13.6      | 2.0–15.7     | 4.7–21.1     | 1.3–7.7      | 1.4–8.5      | 1.3–21.1       |
| CEC   | mean      | 32.7bc        | 44.0ab        | 49.3a        | 53.6a        | 22.0c        | 39.6ab       | 41.9           |
|   | range     | 27.0–41.8     | 29.9–58.9     | 26.5–71.4    | 34.8–69.5    | 7.0–54.4     | 31.7–52.9    | 6.9–71.4       |
| pH  | mean      | 6.5ab         | 6.7a          | 6.4ab        | 6.0bc        | 5.6c         | 6.0bc        | 6.3            |
|   | range     | 5.9–6.9       | 6.2–6.9       | 5.7–6.8      | 5.3–6.3      | 5.2–6.6      | 5.7–6.9      | 5.2–6.9        |
| Exchangeable cation saturation %  |           |               |               |              |              |              |              |                |
| Ca  | mean      | 19.8c         | 17.8c         | 18.3c        | 36.7b        | 53.8a        | 24.9c        | 24.3           |
|   | range     | 13.3–23.5     | 11.2–21.4     | 10.8–21.7    | 27.3–45.2    | 35.7–70.4    | 15.9–32.1    | 10.8–70.4      |
| Mg  | mean      | 78.8a         | 80.8a         | 79.1a        | 61.8b        | 42.5c        | 72.4a        | 73.5           |
|   | range     | 75.1–85.4     | 77.0–87.7     | 71.5–85.0    | 51.7–71.8    | 18.7–61.1    | 65.5–80.3    | 18.7–87.7      |
| Ammonium acetate extractable cations cmol <sub>c</sub> kg <sup>-1</sup> |           |               |               |              |              |              |              |                |
| Ca  | mean      | 6.5b          | 7.8b          | 9.0b         | 20.1a        | 10.9b        | 10.0b        | 9.4            |
|   | range     | 4.5–8.7       | 4.5–11.1      | 4.8–13.7     | 9.5–28.9     | 4.9–21.4     | 5.1–13.7     | 4.5–28.9       |
| Mg  | mean      | 25.8b         | 35.6ab        | 38.9a        | 32.7ab       | 10.6c        | 28.5ab       | 31.6           |
|   | range     | 20.7–32.7     | 24.0–47.4     | 21.3–53.6    | 24.0–40.9    | 1.3–32.5     | 23.5–39.0    | 1.3–53.6       |
| Na  | mean      | 0.0a          | 0.1a          | 0.2a         | 0.2a         | 0.0a         | 0.0a         | 0.1            |
|   | range     | 0.0–0.1       | 0.0–0.3       | 0.1–1.2      | 0.1–0.4      | 0.0–0.1      | 0.0–0.1      | 0.0–1.2        |
| K   | mean      | 0.3a          | 0.4a          | 0.5a         | 0.5a         | 0.3a         | 0.7a         | 0.4            |
|   | range     | 0.2–0.5       | 0.2–0.6       | 0.2–2.1      | 0.1–1.0      | 0.2–0.4      | 0.2–1.5      | 0.1–2.1        |
| Mn  | mean      | 0.1a          | 0.1a          | 0.6a         | 0.1a         | 0.2a         | 0.3a         | 0.3            |
|   | range     | 0.0–0.2       | 0.0–0.4       | 0.1–4.7      | 0.0–0.3      | 0.1–0.3      | 0.1–0.9      | 0.0–4.7        |
| Al  | mean      | 0.00a         | 0.00a         | 0.00a        | 0.00a        | 0.06b        | 0.00a        | 0.01           |
|   | range     | 0.00–0.01     | 0.00–0.00     | 0.00–0.01    | 0.00–0.00    | 0.00–0.23    | 0.00–0.01    | 0.00–0.23      |
| Ni  | mean      | 0.04ab        | 0.04ab        | 0.07ab       | 0.02b        | 0.01b        | 0.06a        | 0.04           |
|   | range     | 0.03–0.07     | 0.01–0.06     | 0.02–0.22    | 0.00–0.04    | 0.00–0.03    | 0.01–0.12    | 0.00–0.22      |
| Ca/Mg   | mean      | 0.26b         | 0.22b         | 0.23b        | 0.61b        | 1.59a        | 0.36b        | 0.43           |
|   | range     | 0.16–0.31     | 0.13–0.28     | 0.13–0.28    | 0.38–0.88    | 0.58–3.77    | 0.20–0.49    | 0.13–3.77      |
| Dithionite extractable metals mg kg <sup>-1</sup>                       |           |               |               |              |              |              |              |                |
| Mn  | mean      | 727b          | 651b          | 1 729ab      | 212b         | 683b         | 3 712a       | 1 251          |
|   | range     | 380–1 050     | 224–1 612     | 227–9 562    | 28–398       | 426–1 023    | 854–12 545   | 28–12 545      |
| Fe  | mean      | 21 079a       | 13 285ab      | 21 475a      | 7660b        | 13 122ab     | 22 713a      | 17 477         |
|   | range     | 13 179–32 378 | 10 261–21 805 | 9 431–76 813 | 4 395–10 480 | 7 633–21 273 | 7 552–44 355 | 4 395–76 813   |
| Al  | mean      | 1 472a        | 691b          | 747b         | 729b         | 1 871a       | 1 660a       | 1 041          |
|   | range     | 666–2 279     | 471–995       | 476–1 123    | 535–1 090    | 1 049–3 561  | 644–2 186    | 471–3 561      |
| Cr  | mean      | 240a          | 99c           | 121bc        | 86c          | 75c          | 200ab        | 131            |
|   | range     | 140–434       | 74–183        | 55–191       | 24–242       | 35–161       | 29–334       | 24–434         |
| Ni  | mean      | 378a          | 353ab         | 483a         | 87bc         | 56c          | 570a         | 365            |
|   | range     | 275–516       | 211–541       | 296–1 233    | 51–152       | 6–143        | 80–1 505     | 6–1 505        |

† Map units within each soil property followed by the same letter are not statistically different at  $P = 0.05$  level. Data was analyzed with the general linear procedure of SAS (SAS, 1987). Separation of map unit means was determined by Tukey's test.

‡ Total C (weight %).

(Rabenhorst et al., 1982; Bulmer and Lavkulich, 1994; Gasser et al., 1995). The higher concentration of  $\text{Al}_e$  in Unit 5 probably results from the concentration of Al in the nonserpentinic parent rock (Table 1).

Nickel<sub>e</sub> concentrations within the study area are low relative to  $\text{Ca}_e$  and  $\text{Mg}_e$ ; however, the mean concentrations of  $\text{Ni}_e$  in Units 1, 2, 3, and 6 are at levels considered to be toxic to plants,  $>0.02 \text{ cmol}_c \text{ kg}^{-1}$  (Vanselow, 1966; Proctor and Woodell, 1975). While mean  $\text{Ni}_e$  values are not significantly different for Units 1, 2, 3, and 6 (Table 3),  $\text{Ni}_e$  is concentrated in the lower landscape positions of Units 3 and 6 (Fig. 6). Nickel is mobile and tends to be leached from the upper part of soil profiles (Gasser et al., 1995). Gasser and Dahlgren (1994) suggested that  $\text{Ni}_e$  increases with organic C and CEC in serpentine soils, however Unit 4 has the largest CEC and C content of all landscape units (Table 3), but has very little  $\text{Ni}_e$

(mean,  $0.02 \text{ cmol}_c \text{ kg}^{-1}$ ). Within this study, the leaching of Ni from upslope and its subsequent accumulation in lower landscape positions is a likely explanation of  $\text{Ni}_e$ .

**Table 4. Average Fe and Mn concentration in soil water collected seasonally (Dec., Mar., June, Sept.) in 1996–1997.**

| Location | Landscape unit | Quantity of lysimeters | Lysimeter depth<br>cm | Mn<br>— mmol L <sup>-1</sup> — | Fe    |
|----------|----------------|------------------------|-----------------------|--------------------------------|-------|
| a        | 1              | 1                      | 90                    | 0.000                          | 0.000 |
| b        | 2              | 3                      | 60, 90, 120           | 0.001                          | 0.000 |
| c        | 2              | 3                      | 60, 90, 120           | 0.000                          | 0.000 |
| d        | 2              | 3                      | 60, 90, 120           | 0.000                          | 0.001 |
| e        | 3              | 3                      | 30, 60, 90            | 0.010                          | 0.012 |
| f        | 3              | 3                      | 30, 60, 90            | 0.019                          | 0.005 |
| g        | 4              | 3                      | 30, 60, 90            | 0.005                          | 0.001 |
| h        | 4              | 3                      | 30, 60, 90            | 0.001                          | 0.001 |
| i        | 5              | 2                      | 60, 90                | 0.000                          | 0.000 |
| j        | 3              | 3                      | 30, 60, 90            | 0.000                          | 0.000 |
| k        | 3              | 3                      | 30, 60, 90            | 0.011                          | 0.003 |

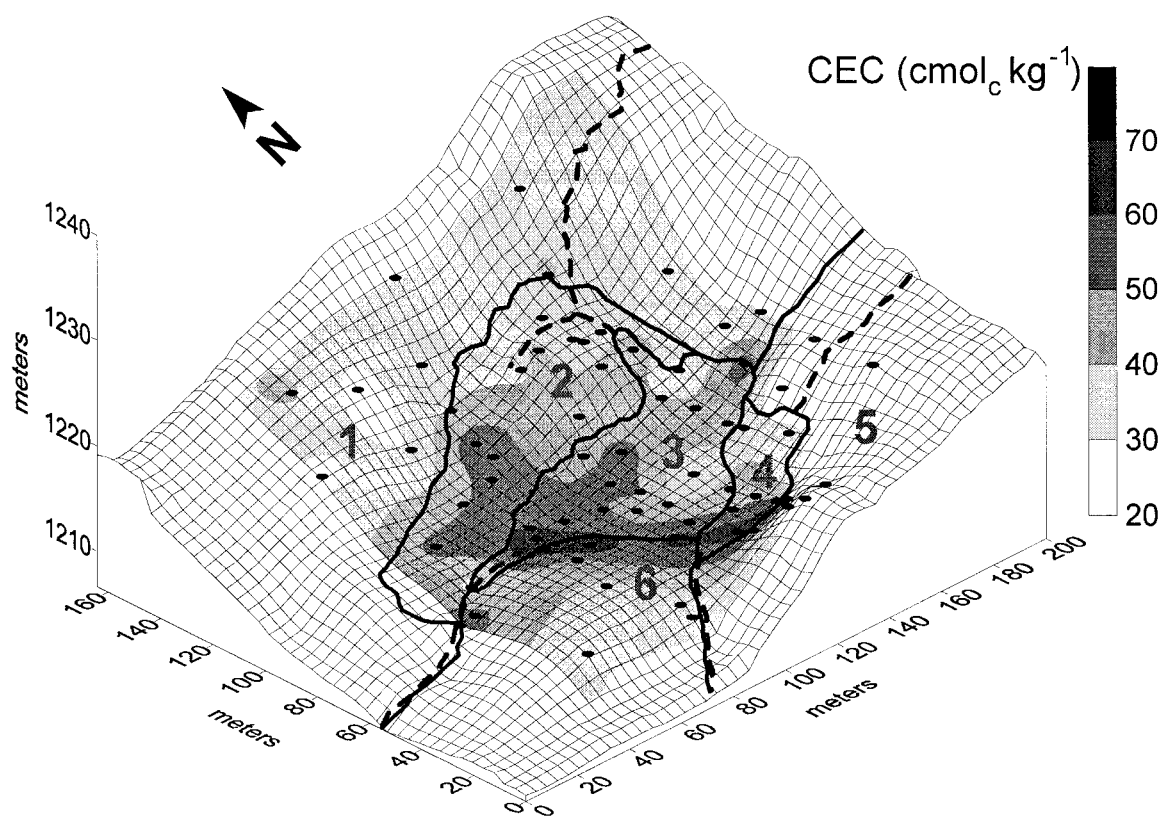


Fig. 4. Spatial distribution of cation-exchange capacity (CEC) in surface soils.

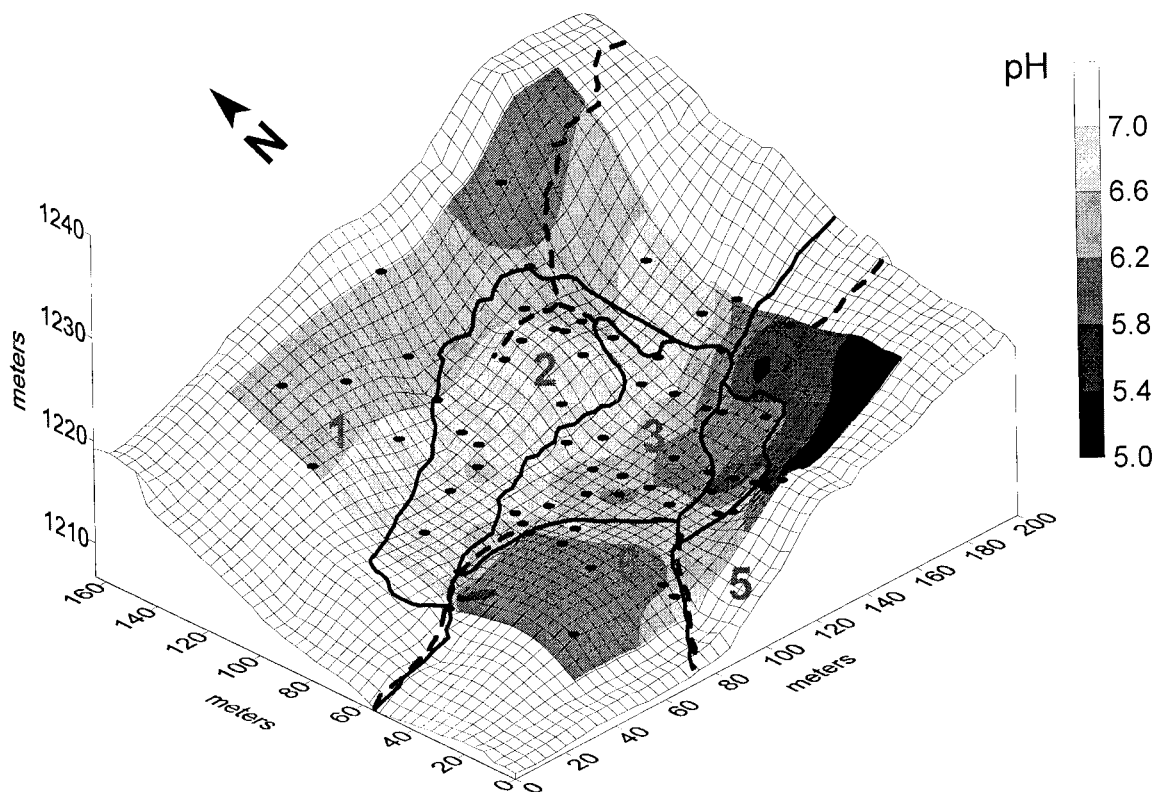


Fig. 5. Spatial distribution of pH in surface soils.

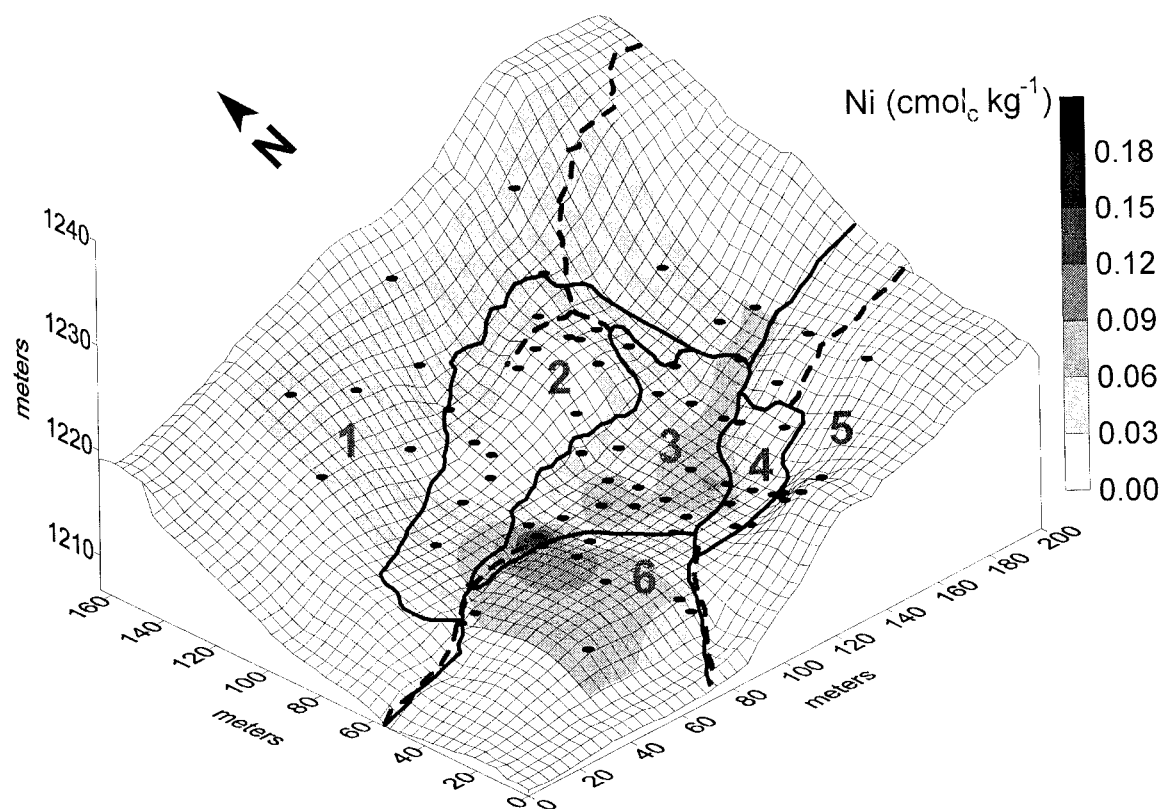


Fig. 6. Spatial distribution of exchangeable Ni in surface soils.

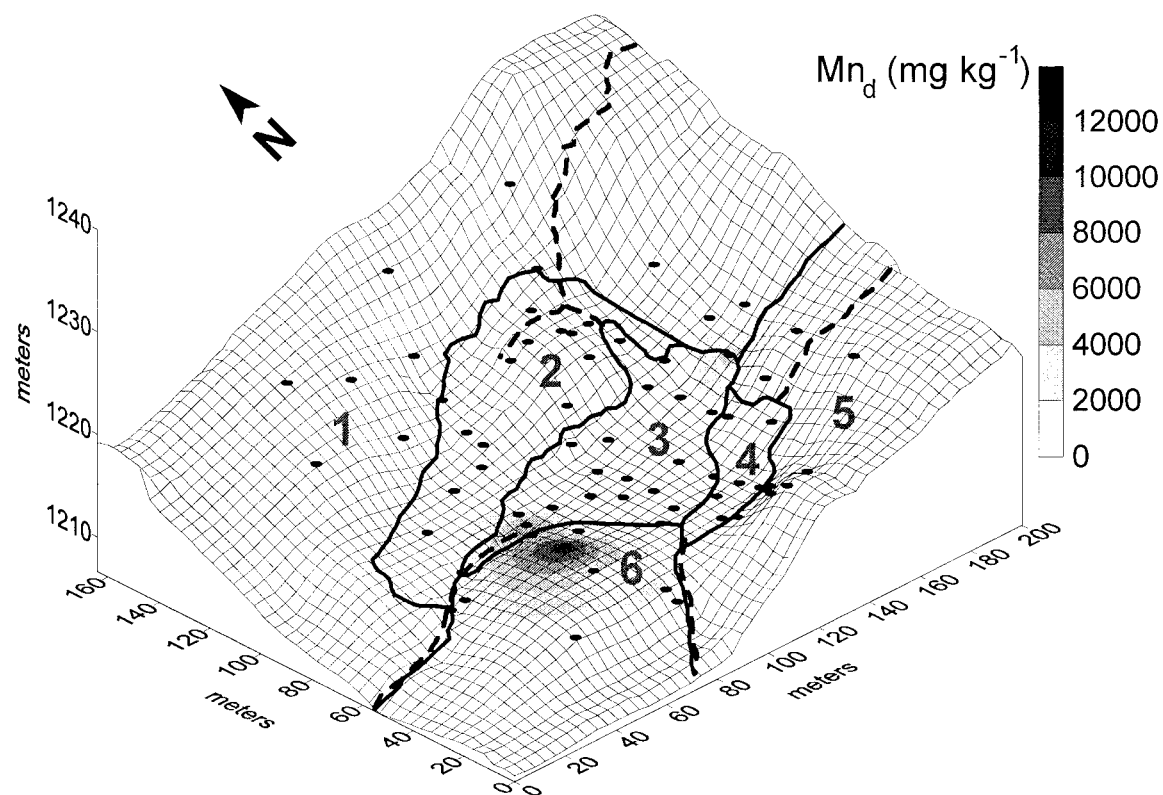


Fig. 7. Spatial distribution of dithionite-extractable Mn in surface soils.

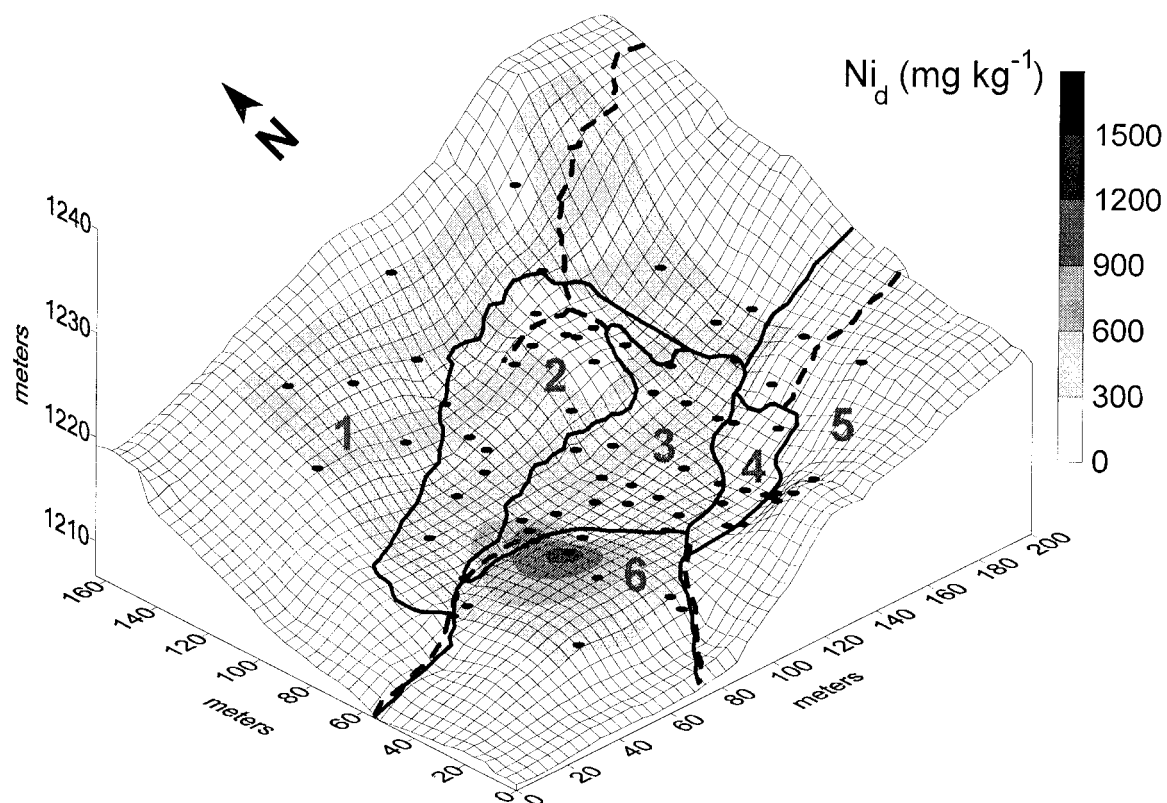


Fig. 8. Spatial distribution of dithionite-extractable Ni in surface soils.

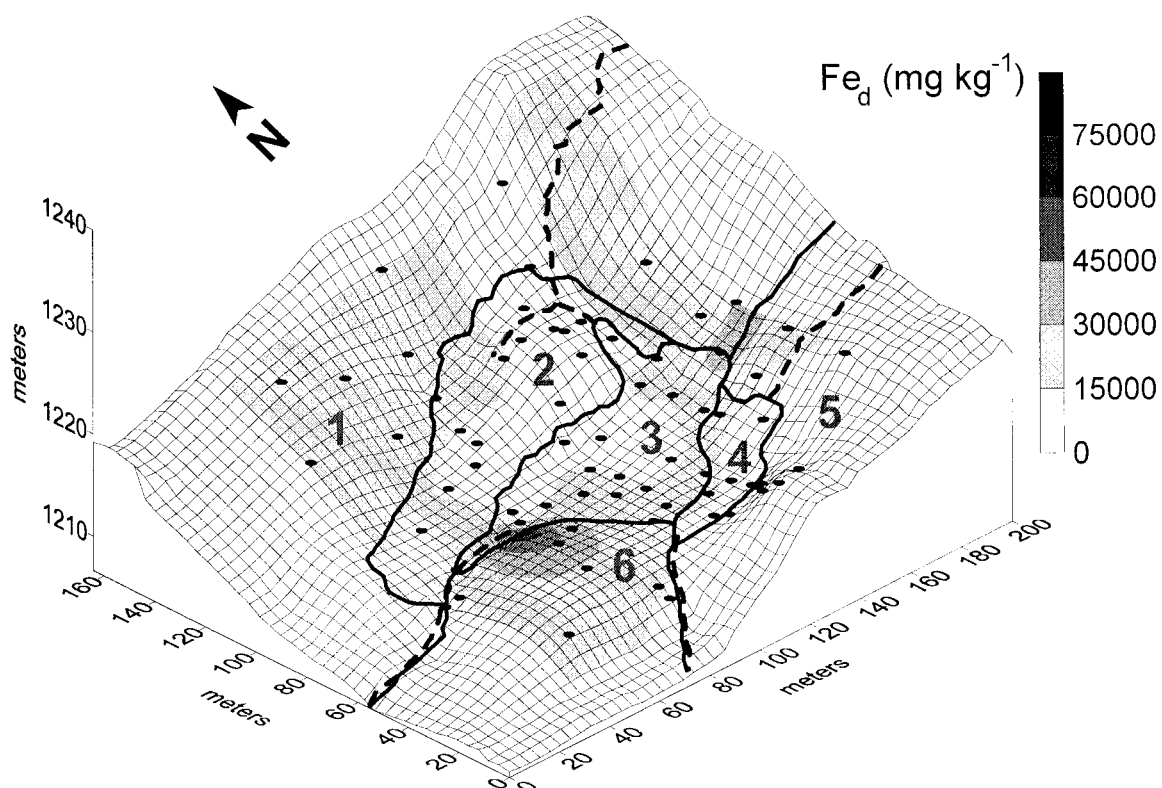


Fig. 9. Spatial distribution of dithionite-extractable Fe in surface soils.

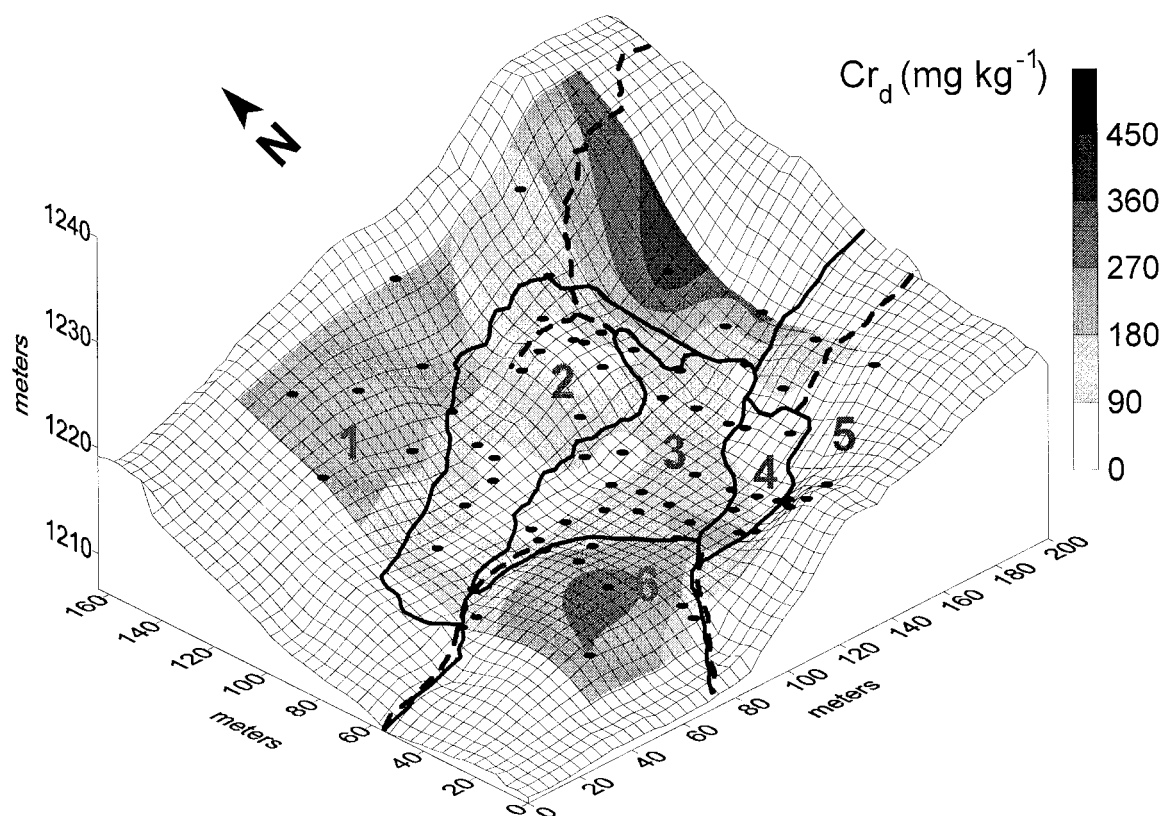


Fig. 10. Spatial distribution of dithionite-extractable Cr in surface soils.

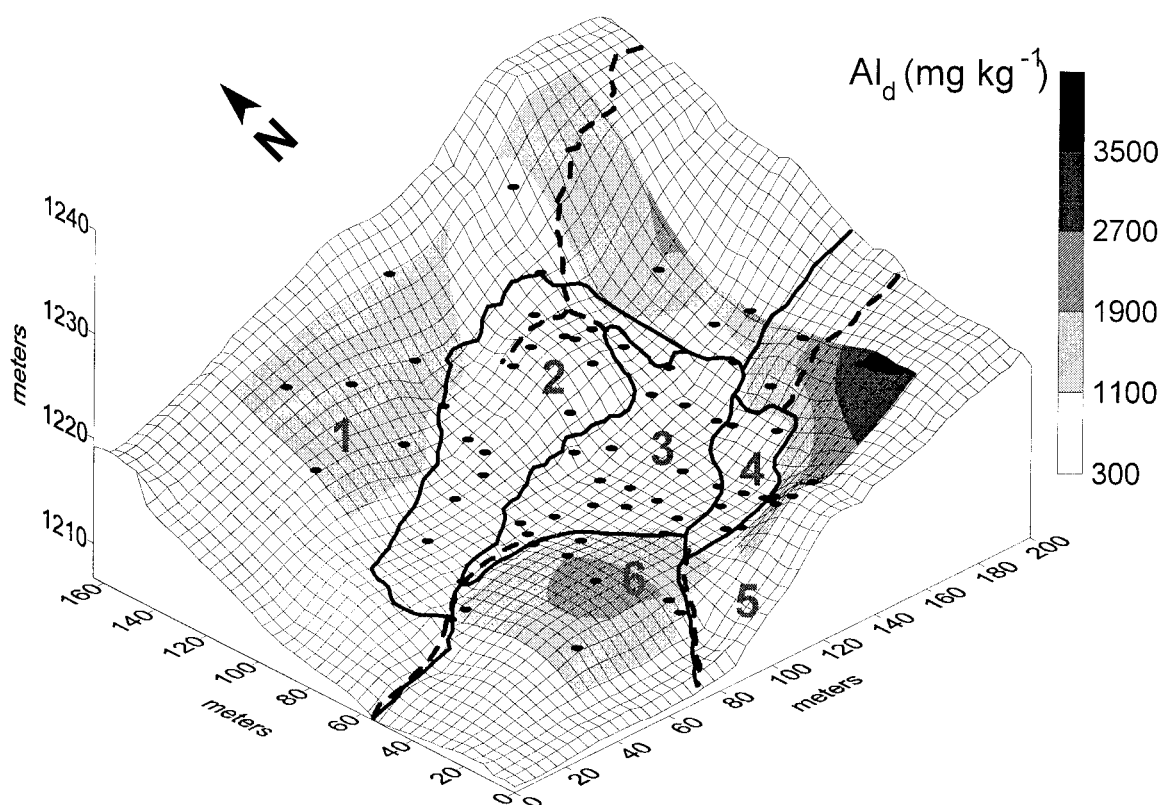


Fig. 11. Spatial distribution of dithionite-extractable Al in surface soils.

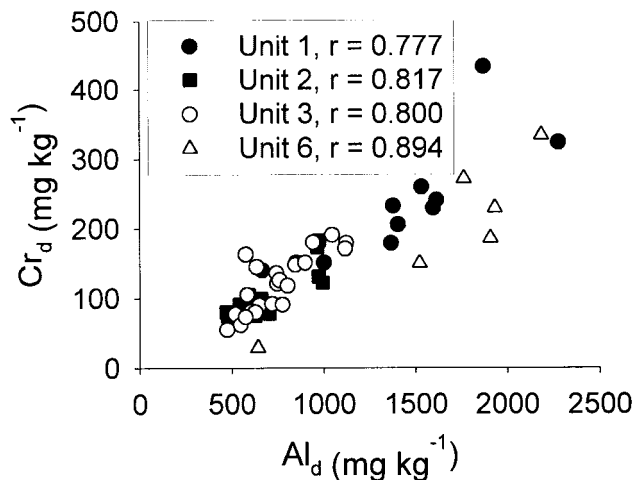


Fig. 12. Correlation of dithionite-extractable Al ( $Al_d$ ) vs.  $Cr_d$  in landscape Units 1, 2, 3, and 6 ( $\alpha = 0.5$ ).

distribution. The low concentration of  $Ni_e$  in Unit 4 is because of its topographic position, downslope of the nonserpentinic Unit 5, where there is little contribution of  $Ni_e$  from upslope leaching.

#### Dithionite-Extractable Metals

The concentrations of  $Fe_d$  and  $Mn_d$  measured in this study are similar to those of surface and near surface horizons of some previously studied serpentine soils (Bulmer and Lavkulich, 1994; Gasser and Dahlgren, 1994; Gasser et al., 1995), but slightly lower than concentrations found in other Klamath Mountain serpentine soils (Alexander et al., 1989). Within the study area, the highest concentrations of  $Mn_d$  and  $Fe_d$  are in the lowest part of Unit 6 adjacent to the wetland (Fig. 7 and 9). Manganese and Fe are redox sensitive elements that are more soluble when in their reduced divalent state. They move with water to low landscape positions where they precipitate in surface horizons of localized oxidizing environments. The relatively high Fe and Mn content in the soil water collected from lysimeters in Units 3 and 4 near the wetland border (Table 4) reflect the mobility and concentration of Fe and Mn in the lower landscape positions.

The  $Ni_d$  concentrations within the study area are similar to those previously reported in serpentine soil studies (Alexander et al., 1989; Bulmer and Lavkulich, 1994; Gasser and Dahlgren, 1994; Gasser et al., 1995). Within the study area,  $Ni_d$  is highest in Unit 6 near the border of Unit 3 (Fig. 8), although the mean concentrations within these units are not significantly different from those in Units 1 and 2 (Table 3). Nickel is commonly adsorbed to Fe and Mn oxides in high pH soils (McKenzie, 1980). Gasser and Dahlgren (1994) found up to 2 mole% of Ni in Fe oxides, and a small amount of Ni in Mn oxides. Hickey and Kittrick (1984) suggested that in most soils ~50% of Ni is in primary minerals, ~20% is in the Fe-Mn oxide fraction, with much of the remainder bound to the carbonate fraction (if present), and only a small proportion in the exchangeable and organic fractions.

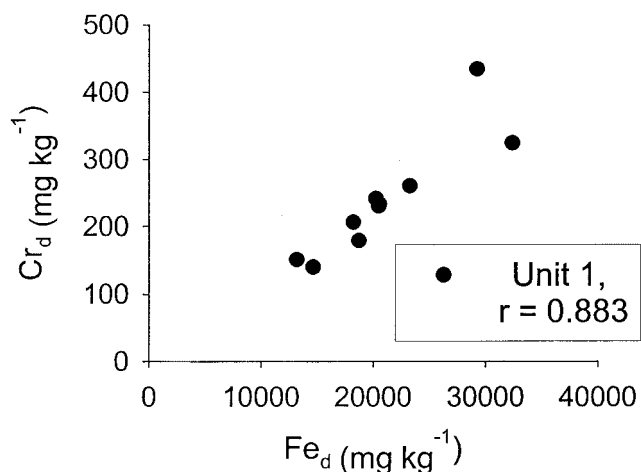
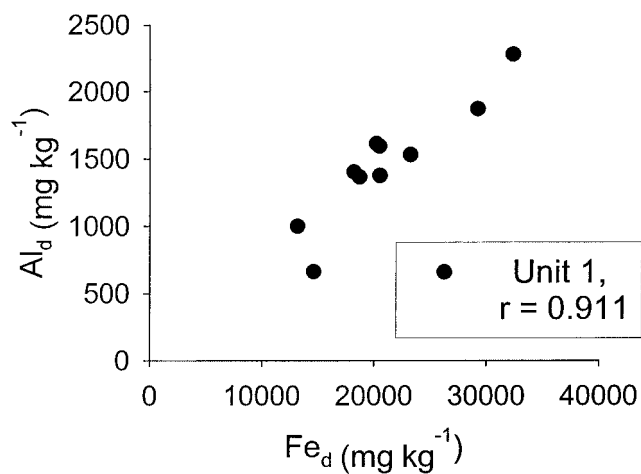


Fig. 13. Correlation of dithionite-extractable Cr ( $Cr_d$ ) and  $Al_d$  vs.  $Fe_d$  in landscape Unit 1 ( $\alpha = 0.5$ ).

The  $Al_d$  and  $Cr_d$  concentrations in the study area are within the range of concentrations reported in previous studies (Alexander et al., 1989; Bulmer and Lavkulich, 1994; Gasser and Dahlgren, 1994; Gasser et al., 1995). Aluminum<sub>d</sub> and  $Cr_d$  distributions are similar in Units 1, 2, 3, and 6 (Fig. 12), consistent with the similar adsorption and solubility behavior noted for these elements by McGrath et al. (1995) and Trolard et al. (1995). Unit 5, formed from nonserpentinic metamorphic colluvium over serpentinic residuum, contains low concentrations of Cr relative to Al possibly due to the difference in parent material. In serpentinic soils, Cr and Al are predominantly in the nonexchangeable fraction (Gasser and Dahlgren, 1994) and considered to be immobile (Wildman et al., 1968; Bulmer and Lavkulich, 1994; Gasser et al., 1995). Chromium is not as soluble as Mn and Ni (Brooks, 1987), therefore it remains upslope with the Fe oxides (Fig. 13). The majority of Cr is in resistant primary minerals, such as spinels (Kanig et al., 1990), however Gasser and Dahlgren (1994) found substitution of Cr in the structure of Fe oxides at 1 mole%.

Aluminum<sub>d</sub> is concentrated in the dry landscape positions surrounding the wetland (Units 1, 5, and 6) (Fig. 11). Serpentine minerals are the main source of Al in serpentinic terrain, and they can contain up to 10 wt. %

Al (Wicks and Plant, 1979). Within Unit 1,  $Al_d$  is significantly correlated with  $Fe_d$  ( $r = 0.911$ ) suggesting that Al may be substituted into the structure of Fe oxides (Fig. 13). Aluminum is commonly incorporated up to 33 mole% into the structure of goethite (Schwertmann and Taylor, 1989). Gasser and Dahlgren (1994) identified an 8 to 11% substitution of Al for Fe in Fe oxides of serpentinitic, mesic Mollic Haploxeralfs.

### Distribution of Vegetation

Unit 5 (south flank) contained a larger diversity of species than Unit 1 (north flank). Although landscapes are similar, the vegetation in Unit 5 was more dense and was dominated by ponderosa pine, white fir, and Douglas fir, not commonly found in serpentinitic terrain. Unit 5 is considered more fertile than Unit 1 because of its significantly higher Ca/Mg ratios (Table 3) (Alexander, 1988; Alexander et al., 1989).

Unit 6 (bulge) contained vegetation (e.g., ponderosa pine; Table 2) that was not typical of Klamath Mountains serpentinitic terrain. However, the Ca/Mg ratios within this unit were not significantly different from those of Unit 1 (Table 3). Because the bulge formed from colluvium from both the north and the south flanks, it probably contains mixed mineralogy of serpentinitic and nonultramafic metamorphic material. Small changes in mineralogy result in vegetative cover that is not typical of serpentinitic terrain.

Within the hydric soils (Units 2, 3, and 4), there are abundant grasses, sedges, and forbs, however there are no living trees and shrubs due to the high water table. Unit 2 contains a large diversity of plants that includes more grass species than Units 3 and 4. This is probably because Unit 2 is saturated at the surface for a shorter duration. Units 3 and 4 are inundated throughout the year and contain similar water tolerant vegetation species.

Large vegetation differences between moisture class coupled with moderate vegetation differences between landscape units with the same moisture class, suggest that vegetation occurrence within the study area is controlled primarily by hydrology, and secondarily by elemental concentrations.

### CONCLUSIONS

Within the wetland and surrounding terrain, the cation exchange is dominated by Mg and Ca (>96%). High Ca/Mg ratios coincide with nonserpentinitic parent material. Concentrations of  $Ni_e$  reach potentially plant toxic concentrations in soils derived from serpentinitic parent material.

The distribution of diethionite extractable within this serpentinitic wetland and surrounding terrain is related to landscape position. Manganese, Ni, and Fe are mobile in the reducing environment of the wetland, and concentrated in the oxidizing landscape position nearest the hydrologic discharge of the wetland. Chromium and Al are less mobile and are concentrated in the dry, upper landscapes surrounding the wetland.

Within this wetland and the surrounding area, both

hydrology and soil chemical composition were important determinants of vegetation occurrence.

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